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Optical study of europium-doped garnet $Sr_3Y_2Ge_3O_{12}$

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Abstract

The optical emission spectrum of a europium structural probe replacing the yttrium in the garnet $Sr_3Y_2Ge_3O_{12}$ has been recorded at liquid nitrogen temperature. Only the $^5D_0 \rightarrow {}^7F_1$ magnetic transition was observed. This is consistent with the octahedral position occupied by the rare earth element in that structure. No evidence for multisite occupation was found, in contrast with other garnets.

1. Introduction

There has been great interest in the past ten years in the optical and magnetic properties of various rare earth compounds with the garnet structure $Re_3A_5O_{12}$ (Re = Y, Gd; A = Al, Ga, Fe) [1–5]. The reasons were

(i) the possibilities of the structure as an efficient laser material as well as its magnetic properties;

(ii) the spectroscopic puzzle created by this structural type itself, as a consequence of the multiplicity of point symmetry sites observed and classified by means of the dye laser site selective excitation technique.

The doping ions were the rare earths Pr^{3+}, Nd^{3+}, Eu^{3+} and Tb^{3+} as well as transition elements such as Cr^{3+}. This technique reveals the complexity of the structural problem, which was not apparent from the classical crystallographic measurements.

Marin *et al.* [6] have recently refined the structure of $Sr_3Y_2Ge_3O_{12}$ using neutron powder diffraction. Since this compound also has a structure of the garnet type it offers a new opportunity to study the rare earth optical properties together with a versatile approach to the garnet structural problem.

2. Synthesis and crystallographic background

$Sr_3Y_2Ge_3O_{12}$ samples doped with 2% molar europium were synthesized by a solid state reaction. The intimately ground mixture of starting materials, present in stoichiometric proportions, were heated in air at 1250 °C for two days. The final product was checked by X-ray measurements and appeared to be single phased, as far as could be discovered by this technique.

As with other garnets, $Sr_3Y_2Ge_3O_{12}$ crystallizes in a body-centred system with eight formula units per unit cell. The space group is $Ia3d$ (O_h^{10}, no. 230). The value of the lattice constant a is 13.078 Å. In this structure, the Sr^{2+} ions are located at the 24c special position (dodecahedral site) where they are each surrounded by 8 oxygen atoms, forming a polyhedron with D_2 point symmetry. The Y^{3+} ions each lie at a 16a position in an "octahedral" site inside a sixfold coordination polyhedron. Consequently, the point symmetry is S_6 (C_{3i}). This is a situation opposite to that in the classical rare earth garnet $Re_3A_5O_{12}$ in which the rare earth atom occupies the D_2 point site [7, 8]. Figure 1, representing the two situations, shows clearly the two different neighbourhoods.

3. Spectroscopic results

The emission spectrum of $Sr_3Y_2Ge_3O_{12}$:Eu^{3+} was recorded at 77 K, using standard techniques. The fluorescence was excited by the blue lines of a cw-argon ion laser. A very simple spectrum was observed, consisting of only two lines for the $^5D_0 \rightarrow {}^7F_1$ magnetic dipole transition at 17 015 and 16 809 cm^{-1} (Fig. 2). No electric dipole transitions were observed, not even the vibronic transitions often accompanying the $^5D_0 \rightarrow {}^7F_2$ hypersensitive transition. Moreover, no other magnetic dipole transitions were observed from higher emitting levels, showing that all the energy was quenched to $^5D_0$. From this rather limited information, we can still deduce some interesting conclusions:

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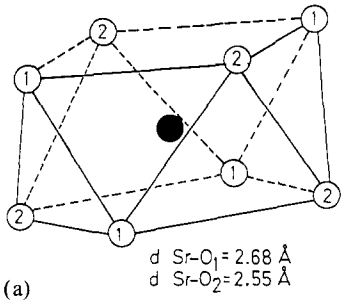
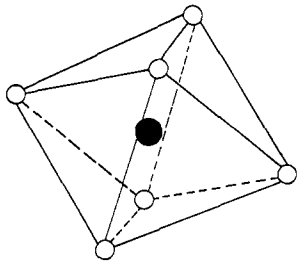


(a)



(b) d Y-O = 2.25 Å

Fig. 1. Coordination polyhedra and interatomic distances for the two types of site in $Sr_3Y_2Ge_3O_{12}$: (a) D_2 site and (b) S_6 site.

(i) The spectrum is consistent with the S_6 point symmetry selection rules for the rare earth ion.

(ii) There is no evidence for extra sites occupied by the rare earths. Of course, we cannot use the site-selective excitation technique for a structure involved in such a small number of allowed transitions. That would be the only way to show the complexity of the garnet problem in the "normal" structural case.

(iii) Although the absolute position of the $^7F_1$ Stark components was not determined, the large splitting of that level (206 cm^{-1}) made it possible to estimate the absolute value of the B_0^2 crystal field parameter as being about 700 cm^{-1}. In addition, the intensity ratio of approximately 1:2 between the two lines, as well as the position of the $^7F_1$ barycentre, allow their attribution to the E and A irreducible representations of the S_6 point group and give a minus sign to this parameter.

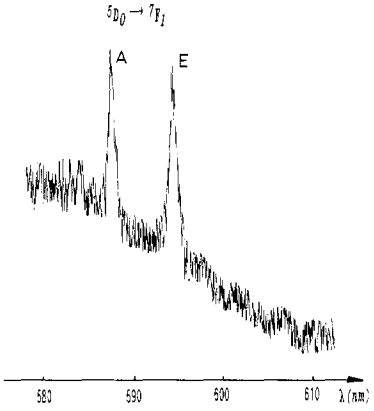


Fig. 2. Emission spectrum of Eu^{3+} in $Sr_3Y_2Ge_3O_{12}$ at 77 K.

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